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The vibrational frequencies of carbon monoxide adsorbed on a platinum metal electrode are obtained in terms of discrete pairwise interatomic interactions. On the one hand, we show that there is a linear dependence of the shift in frequency with uniform linear changes in the binding energy of carbon and oxygen to the surface. Experimental evidence suggests that there is a relationship between the binding energy and the applied electrostatic potential; based on our model, we suggest that the relationship is linear. As a result, we predict a linear dependence of the frequency on electrochemical potential in accord with experiment. On the other hand, we demonstrate that the application of even a relatively large external electric field (of the order of 1×10^9 V/m) has only a minimum effect on the vibrational frequency shift. We conclude that the direct effect of the electrostatic field is unlikely to account for the observed spectral shifts.

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Abstract

The vibrational frequencies of carbon monoxide adsorbed on a platinum metal electrode are obtained in terms of discrete interatomic interactions. We show that for linear changes in the binding energy of carbon and oxygen to the surface there is a linear dependence of the shift in CO vibrational frequency. Based on our model, we suggest that there is a direct, linear relationship between the binding energy and the applied electrostatic potential. As a result, we predict a linear dependence of the frequency on electrochemical potential in accord with experiment. Further, we calculate a Stark tuning rate of 9.0×10^{-9} cm^{-1}(V/m). We also demonstrate that the application of a relatively large external electric field (of the order of 3×10^{9} V/m) is necessary to account for the observed vibrational frequency shift. Because the surface charge of the electrode must change in order to give rise to changes in the electric field, we conclude that a combination of chemical bonding and electric field interactions are required to account for the observed spectral shifts.

Introduction

Among the relatively simple phenomena which have attracted attention, the spectrum of adsorbed carbon monoxide on platinum and other metals has proved to be one of the more interesting. The vibrational spectrum of carbon monoxide adsorbed on a platinum electrode changes as a function of applied electrochemical potential.[1-5] One suspects that, in view of the simplicity of the system, there ought to be some simple, definite, and diagnostic relationship which accounts for the observed linear dependence of the spectral shifts on applied potential. Several interpretations of the experimental results which use several different models have appeared.[3-11] In spite of this variety of treatments of the spectral shift, no single model has yet emerged to enjoy a consensus of support. As the nature of the effect is still an open issue, we offer the following analysis, the results of which agree well with experiment.

Our treatment uses specific, pairwise bond potential energy functions. A cartesian form of symmetry-adapted Taylor series is used to expand the potential functions in order to determine the force constants which are appropriate to the adsorbed carbon monoxide on the metal. We assume that the changes in certain binding energies depend linearly, and directly, upon the applied electrochemical potential. In view of the fact that there is no absolute reference for the electrochemical potential, we assume that there is a linear relationship between the energy of interaction and applied potential. As will be evident in the development of the theory, the functional relationship between the binding energies and the predicted frequencies is non-linear. However, the numerical evaluation of the formulae derived show that the overall, observable dependence of the frequency on the binding energies (D' and c) is linear. As we assume that

the dependence of the binding energies with applied electrochemical potential is also linear, there is agreement with experiment.

The analysis provides insight into the nature of the associations between the atoms of carbon monoxide and the atoms of the metal surface. The theory focuses attention on the loci of points at which the applied electrochemical potential has the greatest influence. In particular, we find that the shifts in frequency can be explained by changes in the strengths of interaction between carbon and the surface and oxygen and the surface; we assume that the CO bond strength is not directly altered by the applied electrochemical potential.

Finally, the suggestion has been made that the spectral shift could be accounted for in terms of an applied external electrostatic field, a Stark effect.[8,10] We have also carried out this type of calculation with the use of our technique. We find that extremely large applied fields, of the order of 1 x 10^8 V/m or greater, are required to affect the spectral shift. It is possible, therefore, that the fields in the double layer can account, at least in part, for the observed phenomenon.

In the following sections we discuss the phenomenon, develop a theory of the spectral shift, and carry out numerical evaluations of the formulae provided by the theory.

The Spectroscopy of Carbon Monoxide on Platinum Electrodes

The vibrational spectrum of carbon monoxide adsorbed on the Pt(111) surface has been extensively studied, using both infrared[12-19] and electron-energy loss spectroscopy.[20-23] When carbon monoxide is adsorbed on a Pt(111) surface under ultra-high vacuum (uhv) conditions, two absorption bands in the C-O stretching

3

region of the spectrum are observed. At low coverage, a band at about 2065 cm^{-1} appears; as the coverage is increased, this band increases in intensity and shifts to higher wavenumber, appearing at about 2100 cm^{-1} at saturation coverage. At intermediate coverage a second band appears at about 1850 cm^{-1}; this band also increases in intensity and shifts to higher wavenumber with further increases in coverage. The comparison of these results with the vibrational spectra of metal carbonyl complexes, together with information on the adsorbate geometry obtained from low-energy electron diffraction experiments[22,24] has led to the generally accepted assignment of the 2065 cm^{-1} band to the C-O stretching mode of carbon monoxide linearly adsorbed at an on-top site, with the carbon end toward the metal, and the assignment of the 1850 cm^{-1} band to carbon monoxide adsorbed in a bridging site, bonded to two, or perhaps three platinum atoms.

The dependence of the wavenumber of the band due to carbon monoxide adsorbed at an on-top site as a function of coverage has been the object of much experimental and theoretical study.[12-19,25-30] Analysis of the infrared spectra of adsorbates formed from mixtures of different isotopes of carbon monoxide has shown that the observed wavenumber shift with coverage is due to dynamical coupling between adsorbed carbon monoxide molecules. The origin of this coupling is not entirely clear, although it has most often been described using a dipole-dipole coupling model.

The infrared spectrum of carbon monoxide adsorbed on a platinum electrode in aqueous solution has also been extensively studied.[1,5] Interpretation of the results obtained from electrochemical systems is necessarily more difficult than for those obtained under uhv conditions. Complex structural changes occur at the surface of an electrode under the conditions of an electrochemical experiment.[31]

and as a result, one has little knowledge of the platinum surface structure. In addition, measurements of coverage on electrodes in solution are more difficult than those carried out in uhv systems. It is also necessary to consider the effect of the presence of the solvent and supporting electrolyte. However, in an electrochemical system, control of the electrode potential provides a valuable method for the study of the adsorbate-surface interaction.

For carbon monoxide adsorbed on a polycrystalline platinum electrode in aqueous acid solution, a band is observed at about 2070 cm^{-1}. By analogy with the uhv results, this solution/surface-phase band has been assigned to carbon monoxide which is linearly bound to an on-top site. A second band at about 1850 cm^{-1} has also been observed and assigned to bridge-bonded carbon monoxide: the intensity of this band is much smaller than that observed under uhv conditions on Pt(111).[5] The 2070 cm^{-1} band appears to be due to the major part of the adsorbate formed in aqueous acid solution, and it has been the most extensively studied. An interesting effect is the behavior of this band as the electrode potential is changed. The band shifts to higher wavenumber as the potential is made more positive. For a saturation coverage of carbon monoxide, the shift is linear with a slope of 30 cm^{-1}/V. This has been interpreted as being due to a decrease in the carbon-oxygen bond strength as electrons are withdrawn into the metal at positive potentials;[3,6] other studies have suggested that this is a minor effect, and that the shift can be explained purely as an electric-field, or Stark, effect.[7,8,32,33] Holloway and Norskov[11] have suggested that the energy and thus the occupancy of the 2π^* antibonding state of the adsorbed molecule changes in response to the external electric field. In addition, these authors predict changes in the binding energy of the carbon monoxide to the surface as the electric potential changes. According to the Gouy-Chapman-Stern (GCS) model

of the double-layer.[34] the electric potential decreases linearly within the first few angstroms of the electrode surface; in this region electric fields of between 10^7 and 10^9 V/m are expected to exist. It has been suggested that the coupling of the adsorbate vibrations with this strong electric field is the source of the observed wavenumber shift with potential. It is also possible that the change in potential causes a change in the dynamical coupling in the adsorbate layer; this possibility has received little attention to date. The behavior of the band at potentials at which CO begins to oxidize depends on the potential at which the adlayer was originally formed. When adsorption is carried out in the double-layer region, the linear 30 cm^{-1}/V shift continues until all of the CO is oxidized to CO_2. When the adsorption of carbon monoxide is carried out at potentials at which hydrogen is coadsorbed, the C-O stretching band decreases in wavenumber when CO begins to oxidize.[9] This effect has been taken as evidence that carbon monoxide is adsorbed in islands in the double-layer region, and that subsequent oxidation at higher potentials occurs at the edges of these islands. Thus, most of the adsorbed molecules that remain experience an effective high-coverage environment. It is thought that coadsorption of hydrogen prevents this island formation, and that oxidation of carbon monoxide at the higher potentials proceeds randomly, thus decreasing the effective coverage near the remaining adsorbed molecules and resulting in a decrease in wavenumber as the coverage-dependent intermolecular coupling decreases.

Analysis of the Spectrum of Adsorbed Carbon Monoxide on Platinum

A model to obtain the spectrum of adsorbed carbon monoxide on platinum is developed in terms of the atoms and associated bonds which are involved. Despite

the abundant experimental evidence for dynamical coupling between carbon monoxide molecules, the model will be limited to a single adsorbed carbon monoxide: an extension of the model to include the effects of intermolecular interactions in the adsorbed layer, as well as the effect of solvent, will be developed in a future paper. The analysis is illustrated in particular with the use of Pt(111). The vibrational analysis is carried out in the classical limit, as is consistent with the usual form of treatment of the lowest order, harmonic vibrations of molecules. The total energy of the system is the sum of the kinetic and potential energies, the Hamilton function.

$$H = T + V \qquad (1)$$

with

$$T = \sum_i p_i^2/2m_i \qquad (2)$$

The summation includes only the carbon and oxygen atoms; platinum vibrations in the surface are not determined, although it is possible to do so.

The potential energy is specifically the sum of the following discrete interactions:

$$V = V_{CO} + V_{CS} + V_{OS} \qquad (3)$$

In this expression, V_{CO} is a Morse potential which represents the underlying bonding in carbon monoxide.

$$V_{CO} = D \exp[a(r_{CO}^0 - r_{CO})]\{\exp[a(r_{CO}^0 - r_{CO})] - 2\} \qquad (4)$$

The values of D, a, and r_{CO}^0 are those for an isolated carbon monoxide molecule: r_{CO} is the carbon-oxygen separation. The function V_{CS} describes the interaction

of carbon with the surface. We used a Lennard-Jones potential for the interaction of the carbon atom with each of the surface atoms, so V_{CS} is the sum

$$V_{CS} = \epsilon \Sigma_i [(c/r_{ci})^{12} (c/r_{ci})^6 - 2]$$
(5)

In which the radii r_{ci} are the distances between the carbon atom and each platinum atom i. The model of the platinum surface consists of 14 platinum atoms arranged in a (111) configuration (cf., Figure 1). The last term in the potential, V_{OS}, represents the oxygen-surface interaction. We used a sum of Morse potentials for each of the oxygen atom-surface atom interactions.

$$V_{OS} = \Sigma_i D'\exp[\gamma(|r_{oi} - r_{ai}|)](\exp[\gamma(|r_{oi} - r_{ai}|)] - 2]$$
(6)

In which the r_{oi} are the distances between the oxygen atom and each platinum atom.

The calculations to derive the force constants, from which the vibrations of carbon monoxide are determined, require the use of a two-center form of the Taylor series. This follows as the potential energy function for the system is a sum of pairwise interactions. A symmetry-adapted form of Taylor series, which has been used elsewhere.35-47 proves to be the easiest to work with.

Given a scalar function, which can be expressed as

$$F(r) = Y_{00}(\hat{r})(/4\pi g(r)).$$
(7)

In which $Y_{lm}(\hat{r})$ is the spherical harmonic function, we want to find an expansion about two centers, A and B. separated by a vectorial distance R   A Taylor

series expansion about two centers is given by

$$F(R + a - b) = \Sigma_n (n!)^{-1}(a \cdot \nabla + b \cdot \nabla)^n F(r).$$
(8)

Define the Fourier transform of F(r) as

$$F(r) = \frac{1}{(2\pi)^3} \int d^3k\, f(k)\, e^{-ik \cdot r}$$
(9)

Substitution of this quantity in eq (8), followed by expansion and manipulation of the various expressions yields

$$F(R+a-b) = (4\pi)^2 \Sigma_n 1/n! \Sigma_{s=0}^n \binom{n}{s} a^{n-s}(-b)^s \Sigma_{(l,m)} [(2l_1-1)!(2l_2-1)!(2l+1)]^{\frac{1}{2}}$$

$$\times (l_1 l_2 00|l0)(l_1 l_2 m_1 m_2|lm) A_{n-s,l_1} A_{s,l_2} Y_{l_1 m_1}(\hat{B}) Y_{l_2 m_2}(\hat{B}) Y_{lm}^*(\hat{R})$$

$$\times I_{nl}(R)$$
(10)

In which $(l_1 l_2 M_1 M_2; LM)$ is a Clebsch-Gordan coefficient. [48] $\binom{n}{s}$ is the binomial coefficient, and A_{nl} is given by[37]

$$A_{nl} = \frac{n!(2l+1)}{(n-l)!!(n-l-1)!!} \quad \text{for } n \geq l \text{ and } n - l = \text{even}$$

$$= 0 \quad \text{for } n < l \text{ and } n - l = \text{odd}$$
(11)

and $I_{nl}(R)$ is

$$I_{nl}(R) = \frac{(-1)^{n-l}}{(4\pi)^{\frac{1}{2}}} R^l (d/RdR)^l (1/R)(d/dR)^{n-l} Rg(R)$$
(12)

Alternative integral representations of this quantity exist   Indeed, the differential form, eq (12), is obtained from the integral form   For the Morse potential, for example, one finds

$$I_{n1}(R) = D e^{aR_0}[2^n R\, k_{n-1}(2aR) - (n-1)k_n(2aR)]$$
$$- 2[aR\, k_{1-1}(aR) - (n-1)k_1(aR)]]$$

(13)

In which $k_n(x)$ is the modified spherical Bessel function of the third kind.[49]

The cartesian form of the first and second order terms in this expansion are the most directly useful in our analysis. One can write for the first order term (which is useful in the process of finding the optimum configuration of the system)

$$g_1(R \rightarrow a \rightarrow b) = \sqrt{4\pi}[(a - b)\cdot R]I_{11}(R)/R$$

(14)

In which $I_{11}(R)$ is given simply by

$$I_{11}(R) = (4\pi)^{-\frac{1}{2}} \frac{dg}{dR}$$

(15)

For the second order term, one finds

$$g_2(R \rightarrow a \rightarrow b) = \frac{1}{2}(a - b)^T K(a - b)$$

(16)

In which v^T is the transpose of the column vector v. The cartesian diagonal elements of the force constant matrix K are

$$k_{11} = -\frac{1}{3}(4\pi)^{\frac{1}{2}}[I_{20}(R) + (2x_1^2 - x_j^2 - x_k^2)I_{22}(R)/R^2]$$

(17)

where X_i is the i-th cartesian component (i=x,y,z) of the vector R between the centers A and B. The cartesian off-diagonal elements are

$$k_{ij} = \sqrt{4\pi}\, X_i X_j I_{22}(R)/R^2$$

(18)

The radial quantities $I_{20}(R)$ and $I_{22}(R)$ are specifically

$$I_{20}(R) = \frac{2}{R}\frac{dg}{dR} - \frac{d^2g}{dR^2}$$

(19)

and

$$I_{22}(R) = \frac{d^2g}{dR^2} - \frac{1}{R}\frac{dg}{dR}$$

(20)

For the Morse potential, the radial quantities I_{20} and I_{22} are specifically

$$I_{20}^M(R) = 2a^2 D_e e^{a(R_0-R)}[2e^{a(R_0-R)}(1-1/aR) - 1 + 2/aR]$$

(21)

and

$$I_{22}^M(R) = 2a^2 D_e e^{a(R_0-R)}[e^{a(R_0-R)}(2-1/aR) - 1 - 1/aR]$$

(22)

In the limit as $R = R_0$, these quantities reduce to

$$I_{20}(R) = I_{22}(R) = 2a^2 D$$

(23)

For the Lennard-Jones potential, we find for I_{20} and I_{22}:

$$I_{20}^{LJ}(R) = \frac{12\epsilon}{R^2} (c/R)^6[11(c/R)^6 - 5]$$

(24)

and

$$I_{22}^{LJ}(R) = \frac{24\epsilon}{R^2} (c/R)^6[7(c/R)^6 - 4]$$

(25)

In the limit, in these equations, as $R = R_0 = c$,

$$I_{20} = I_{22} = 72\epsilon/c^2$$

(26)

Examination of eq (10) indicates that there are two kinds of second order contribution to the force constant matrix. The first kind of contribution arises when n = 2 and s = 0.2. These, of course, are the only allowed values for s in this limit. One sees without much difficulty, that for these values of the indices, the contributions to the force constant matrix become diagonal in the species index. In effect, these cartesian force constants correspond to the

oscillation of an atom A in the static field of the surroundings: the vector R_{ab} connects the particle A with B, but the displacement of B does not enter at this point. If the complete potential energy function is a sum of pair potentials, then for species A there is a sum of contributions to the overall force constant due to the interaction with all surrounding species.

The other term which arises, appears for $n = a = -1$. In this instance, the cartesian elements of the force constant matrix are nondiagonal in the species indices. That is, the cartesian displacements of species A are coupled bilinearly with those of species B. There are only two of these dynamical interactions for each pair of particles; the summation of course is divided by 1/2 to avoid double counting.

Because of the nature of the contributions for $n = 2$, $s = 0.2$. It is possible to see that environmental effects can enter the vibrational analysis in a direct and simple manner. For the example of carbon monoxide adsorbed on platinum, which is the subject of this report, it is easy to see that a major environmental effect is the interaction of the atoms of carbon and oxygen with the atoms of platinum both in the surface and, if warranted, below the surface. All that is needed is an appropriate form of potential energy function for which it is possible to obtain the quantities $I_{20}(R)$ and $I_{22}(R)$.

Method and Results

The parameters in the expression for the interaction potential are listed in Table 1. We arbitrarily chose the parameters in V_{CO} to be those for gas-phase carbon monoxide. The parameter r_{01} in V_{OS} was chosen to make this a repulsive term; the remaining parameters in V_{CS} and V_{OS} were optimized by a least squares

fit to the experimental binding energies and the carbon-oxygen and platinum-carbon vibrational frequencies as found under uhv conditions for carbon monoxide bonded both to on-top and bridging sites. The values derived from the empirical potential are listed in Table 2 along with the experimental values. Complete C-O and Pt-C bond length optimization were performed at each site by the Newton-Raphson method. The geometry was optimized with carbon monoxide bound normal to the surface, with the carbon end towards the metal. The binding energy was calculated as the difference between the total energy from eq(3) and the dissociation energy of isolated carbon monoxide. The parameters in the V_{CS} and V_{OS} parts of the potential were refined until the calculated binding energy and vibrational frequencies gave acceptable agreement with experiment. A similar calculation has been attempted using the Morse potential for the CO interaction but Lennard-Jones potentials for both V_{CS} and V_{OS}. It was found that because of the steep repulsive wall in the Lennard-Jones potential, the CO stretching frequency was perturbed too strongly. The parameters were easily optimized for either the on-top site or the bridging site, however, a set of parameters to satisfy both conditions could not be found. In addition, the binding energy was in poorer agreement with experiment.

The potential energy surface for carbon monoxide adsorbed at an on-top site of Pt(111), as calculated with eq (3) using the optimized parameters, is shown in Figure 2. The zero of energy is chosen with reference to carbon monoxide in the gas phase. The binding energy which is calculated from this potential energy function is 2.4 eV; this is about twice that which is observed experimentally.[90] This is due to the fact that we used parameters appropriate for gas-phase carbon monoxide in V_{CO}, so that in order to match the experimentally observed frequencies for adsorbed carbon monoxide, we have over-estimated the strength of

the surface-adsorbate interaction. Of course, the bond between carbon and oxygen should change when CO is adsorbed, but we have neglected this effect since we were only interested in the change in the vibrational frequencies with changes in binding energies. The calculated frequencies are consistent with the experimental frequencies[3,51] cf. Table 2. Figure 3 represents the interaction potential for lateral carbon monoxide motion across the platinum surface. With reference to this surface, the most stable configuration is found to be the on-top site, with binding energy of about 2.4 eV, followed by the bridging site with binding energy of about 2.3 eV. The relative stabilities agree well with experiment. Nevertheless, it should be borne in mind that this is only an approximate energy surface; only qualitative conclusions should be drawn. However, in this analysis we are interested in regions of the surface very near the equilibrium C-O and Pt-C bond distances. As the vibrational data obtained from the interaction potential agree well with experimental data, the surface should be a reasonable initial approximation to the actual surface in this limited region. We confine our attention to this region of the surface in order to explore the relative contributions to the potential-dependent CO frequency shift from the chemical bonding and Stark type mechanism.

The energy quantities, D' in the oxygen-surface and ϵ in the carbon-surface potential, were changed linearly. The resulting frequencies responded linearly to these changes. cf. Figures 4 and 5. Table 3 lists the vibrational frequencies and the equilibrium C-O and Pt-C bond distances as a function of binding energy. The potential dependence of the Pt-C vibrational frequencies is included in Table 3, although this has not yet been measured. The size of the shift in wavenumber which was calculated for this range of binding energies is about the same as that observed experimentally.[4] cf. Table 3.

Finally, the system was perturbed with an electric field by adding the new quantity V_{field} to the interaction potential:

$$V_{field} = E_z M(z'-z). \qquad (27)$$

The purpose of the perturbation was to see if a Stark effect could be seen. A potential of this type is consistent with the Gouy-Chapman-Stern theory of the electrical double layer.[34] In this expression E_z is the electric field strength in a direction normal to the surface. M is (du/dz) obtained from expansion of the dipole moment function, and the term $(z'-z)$ is the relative displacement of the atom from its equilibrium position (z') in a direction normal to the surface. The experimental value of (du/dz) for CO in gas phase is 3.093 D/A.[52] Lambert has found that this value increases by about a factor of 2 when CO is adsorbed on Ni(110).[8] Therefore, to calculate the electric field perturbation we have taken (du/dz) to be 6.18 D/A. Using this model, we calculate a Stark tuning rate of 9.0×10^9 cm^{-1}(V/m) in excellent agreement with Lambert.[8]

The vibrational frequencies of carbon monoxide in the presence of an electric field are shown in Table 4. Figure 6 shows the linear relationship between the frequency shift and the electric field. The electric fields which were used were on the order of those expected from the Gouy-Chapman-Stern model of the double layer. Fields as large as 3×10^9 V/m are required to induce the observed 30 cm^{-1}/V frequency changes. Although these fields are high, they are not unreasonable for an ideal layer of adsorbed carbon monoxide across which the entire electric field drop occurs.

Discussion

The shift of the carbon-oxygen stretching frequency with potential in

perturbation of the CO stretching frequency by an external electric field has been obtained from electroreflectance vibrational spectroscopy (EVS) [32,33] In EVS, a modulated electric field is applied across a pair of metal surfaces. Absorption bands which change in response to the modulated field appear in the final spectrum. However, an electric field between two metal plates depends upon the accumulation of charge on the surfaces of the conductors. Because of the presence of electronic surface charge it is difficult to separate electric field perturbations from changes in chemical bonding between the adsorbate and the metal in an experiment of this type.

In summary, we have constructed a model of adsorbed carbon monoxide on platinum in which the interaction between the molecule and the metal surface is represented in terms of several individual components. We have carried out a second order Taylor series expansion of the complete potential in order to determine the vibrational frequencies for carbon monoxide in the presence of the metal. We have calculated a Stark tuning rate for CO adsorbed on Pt(111) which is in good agreement with that observed for CO on Ni(110). Electric fields greater than 10^9 V/m can contribute significantly to the potential dependent frequency shift. Further, by linearly changing the specific binding energies (which are parameters within these potential energy functions), we have been able to show a linear response in the spectral shift. If one can assume that the change in binding energy also follows a linear change in the electrochemical potential which is applied to the surface, then, we assert, there is excellent accord with experimental results.

adsorbed carbon monoxide appears to be caused by changes both in the electric field and the surface-adsorbate bonding. It should be noted that to simulate changes in bonding it was not necessary to change any of the parameters in the carbon-oxygen potential function to obtain a linear shift with binding energy; only the energies involving the surface-adsorbate interaction (i.e. the energies ε and D' within the potential energy functions) were changed. We calculated that the stretching frequency for carbon monoxide increases linearly as the surface-adsorbate binding energy decreases. The carbon-oxygen stretching frequency in adsorbed carbon monoxide increases towards the value which is known for the free molecule as the potential is increased. Therefore, we think it is reasonable to assume that there is a decrease in the binding energy with increasing potential. Because the experimental frequency is observed to vary linearly with applied electrode potential, within the limits of our model, our results strongly suggest a linear relationship between the binding energy and the electrode potential.

Potential energy surfaces have been derived with the use of several potential energy functions. 6,53,54 Tully[55] has constructed potential energy surfaces for carbon monoxide on Pt(111) in order to study gas phase dynamics. Although not the same as Tully's potential, our potential duplicates the important features. In addition, Tully's potential is easily adapted to this method.

An advantage of the type of analysis reported in this paper is that external perturbations to the potential energy are easily calculated. From this analysis it appears that changes in the vibrational frequency with potential depend upon changes in the binding of carbon monoxide to the platinum surface and on the Stark effect if high enough fields are applied. Experimental evidence for

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Table I. Parameters in the interaction potential

V_{CO} D = 11.11 eV
            a = 2.31 A^{-1} r_{CO}° = 1.13 A

V_{CS} ϵ = 2.04 eV
            c = 1.61 A

V_{OS} D' = .13 eV
            γ = .86 A^{-1} r_{O1}° = 4.6 A

Table II. Values calculated from the interaction potential for CO bonded to on-top and 2-fold bridge sites. Numbers in parentheses are references.

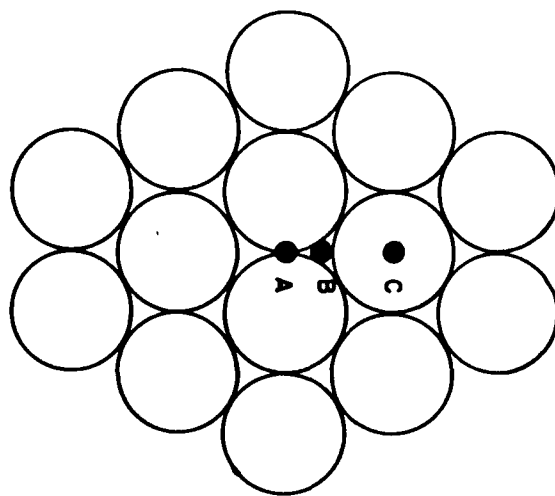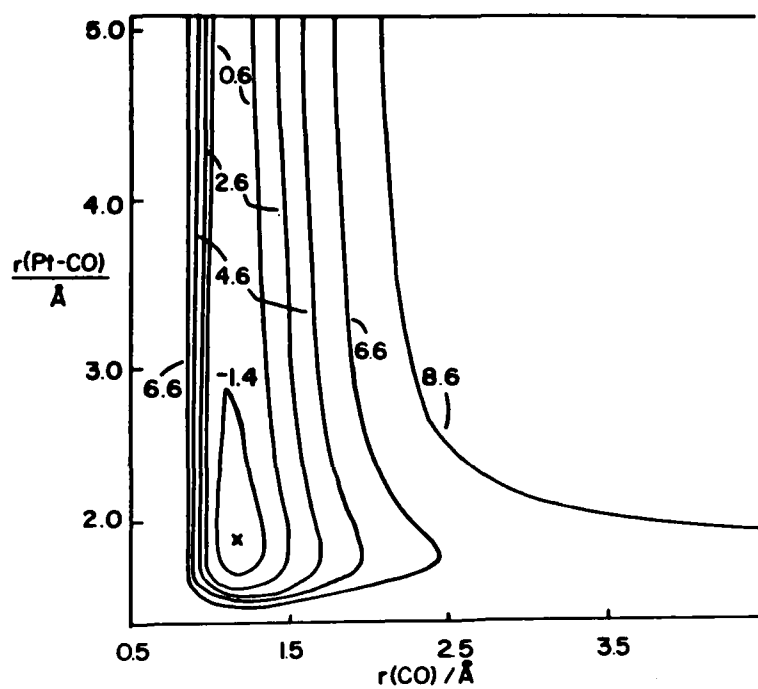|	SITE	r_{C-O}	r_{Pt-C}	ν_{CO}	ν_{Pt-C}	Binding Energy
		(A)	(A)	(cm^{-1})	(cm^{-1})	(eV)
Calculated	TOP	1.16	1.89	2051	456	2.4
	BRIDGE	1.17	1.66	1892	385	2.3
Literature	TOP	---	---	2065 (6)	480 (51)	1.2 (49)
	BRIDGE	---	---	1872 (6)	350 (51)	1.2 (49)

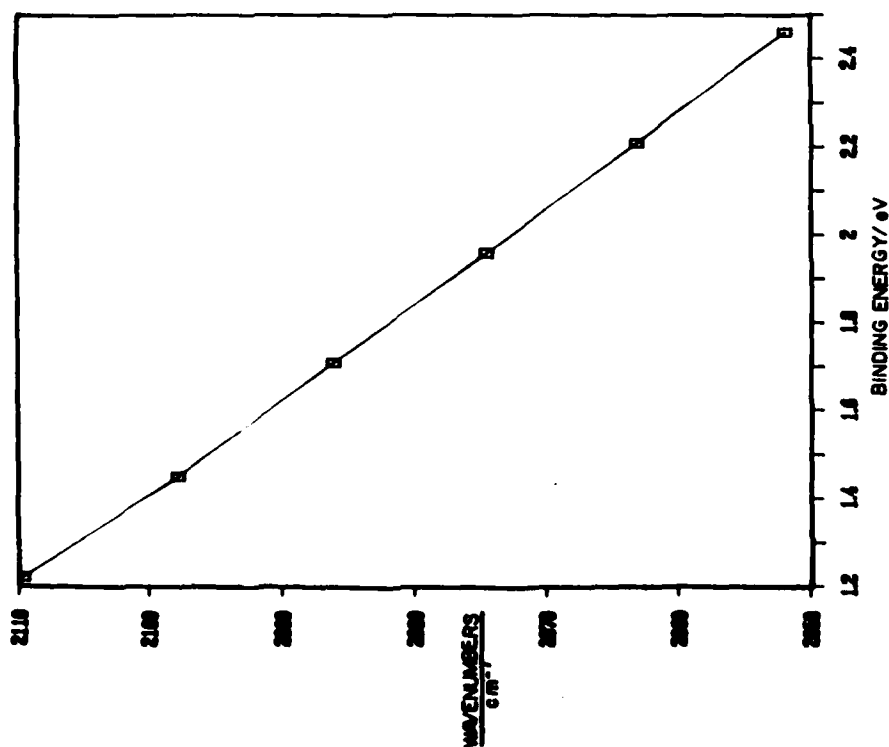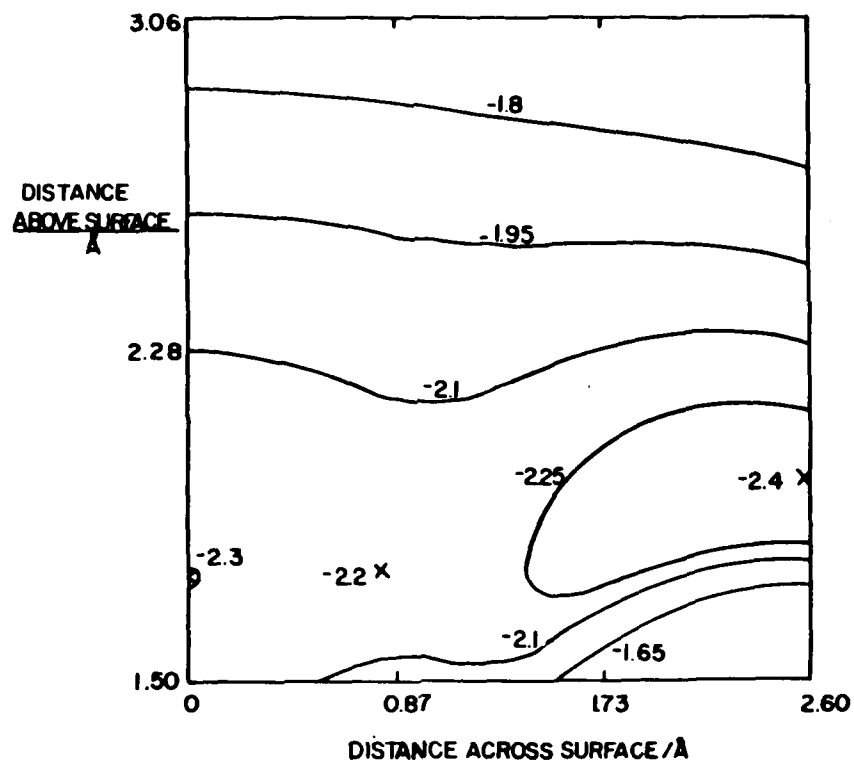## Table III. Values calculated from the interaction potential perturbed by changes in dissociation energies.

D'	r_{C-O}	r_{Pt-C}	ν_{CO}	ν_{Pt-C}	Binding Energy
(eV)	(A)	(A)	(cm^{-1})	(cm^{-1})	(eV)
.125	1.16	1.89	2052	450	2.4
.112	1.15	1.89	2053	434	2.2
.100	1.15	1.89	2075	409	2.0
.087	1.15	1.89	2086	382	1.7
.075	1.15	1.89	2097	352	1.5
.062	1.14	1.89	2110	321	1.2

Table IV. Values calculated from the interaction potential perturbed by an electric field.

Field/	r_{C-O}	r_{Pt-C}	ν_{CO}	ν_{Pt-C}	Binding Energy
10^8 V/m	(A)	(A)	(cm^{-1})	(cm^{-1})	(eV)
0.0	1.15	1.89	2052	459	2.4
2.0	1.15	1.89	2053	459	2.4
4.0	1.15	1.89	2057	459	2.4
6.0	1.15	1.89	2048	458	2.4
8.0	1.16	1.89	2048	456	2.4
10.0	1.15	1.89	2060	458	2.4

Figure Legends

Figure 1. Arrangement of atoms to form the Pt(111) model surface used in this calculation. The nearest neighbor Pt-Pt distance was taken as 2.774 A. A,B, and C represent 2-fold bridge, 3-fold bridge and on-top sites respectively.

Figure 2. Potential energy surface calculated from the adsorbate-surface interaction potential eq(3). Carbon monoxide is bonded to an on-top site on Pt(111).

Figure 3. Potential energy surface calculated from the adsorbate-surface interaction potential eq(3) for motion of carbon monoxide laterally across the platinum surface. The 2-fold bridge site corresponds to the zero of distance across the surface. From left to right the X's correspond to CO interaction with the 2-fold, 3-fold, and ontop sites.

Figure 4. Plot of the carbon monoxide vibrational frequency against the binding energy which acts between carbon monoxide and the platinum surface.

Figure 5. Plot of the Pt-C vibrational frequency against the binding energy which acts between carbon monoxide and the platinum surface.

Figure 6. Plot of the carbon monoxide vibrational frequency against the applied electric field strength.

DISTANCE
ABOVE SURFACE
Å

DISTANCE ACROSS SURFACE /Å

BINDING ENERGY/ eV

WAVENUMBERS
cm⁻¹

WAVENUMBERS
cm⁻¹

BINDING ENERGY / eV

WAVENUMBERS
cm⁻¹

ELECTRIC FIELD / V M⁻¹

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